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Solar photocatalytic disinfection of water with immobilised titanium dioxide in re-circulating flow CPC reactors

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ABSTRACT

It is estimated that 780 million people lack access to improved water supplies and many more are forced to rely on sources that are microbiologically unsafe. While piped-in water supplies are the ultimate goal for the provision of water in developing countries, low cost point-of-use disinfection treatments could help to significantly reduce the incidence of water borne disease. Solar disinfection of water (SODIS) is a simple method of treating water where the UV and thermal energy of the sun act to inactivate pathogenic microorganisms in water; however, the recommended protocol is 6 h under direct sunlight, the efficiency depends on environmental factors, and some pathogens are more resistant to solar disinfection.

The use of compound parabolic collectors (CPC) and immobilised titanium dioxide for photocatalysis were investigated as enhancement technologies for solar disinfection. The reactors consisted of borosilicate glass tubes (1.5 m in length) as either single tubes of diameter 50 mm or two concentric tubes (inner tube of diameter 32 mm) with and without CPC. For solar photocatalytic disinfection (SPC-DIS), the inside wall of the 50 mm tube was dip coated with TiO_2 (TiO_2, *Evonik P25*) and/or the outside wall of the 32 mm tube. SPC-DIS and SODIS were tested under flow conditions using different reactor configurations under real sun conditions. *E. coli* was used as the model microorganism for the disinfection studies in 0.9% saline solution and the total volume in each experiment was 7 L. It was found that the use of CPCs improved the SODIS and SPC-DIS efficiency. The disinfection kinetics were observed to follow a log-linear with shoulder and/or tailing model. The kinetic parameters were determined using the UVA dose as the independent variable and the configurations were compared for *E. coli* inactivation efficiency based on the log of the residual concentration ($\text{Log } N_{res}$) and the first order rate constant (k). Three reactor configurations showed a residual bacterial count below the detection limit and they were compared based upon the first order rate constant. The concentric tube arrangement (a tube within a tube) with CPC was the most effective configuration. The following order was found for k where coated refers to TiO_2 coating and the equals sign indicates no significant difference; uncoated external – coated internal $\geq$ double coated tube $\geq$ uncoated double tube. It is known that *E. coli* is inactivated by SODIS and it may be a 'soft' target for comparing the effectiveness of SODIS vs SPC-DIS. Nevertheless, photocatalysis presents advantages in terms of the non-recovery of inactivated organisms and the inactivation of SODIS resistance organisms.

1. Introduction

The availability of safe drinking water is a high priority issue for human existence and quality of life. Globally, water resources are coming under increasing pressure due to population growth, over-use and wastage. Since the adoption of the Millennium Development Goals, the WHO/UNICEF Joint Monitoring Programme for Water Supply and Sanitation has reported on progress towards achieving Target 7c: reducing by half the proportion of people without sustainable access to safe drinking water and basic sanitation. As of 2012, the target for drinking water has been met; however, it still remains that 780 million people are without access to an improved drinking water source and many more are forced to rely on sources that are microbiologically unsafe [1]. The lack of access to safe drinking water resources results in a higher risk of waterborne disease in humans, including typhoid, hepatitis and cholera [2–4]. In developing countries polluted water sources and inadequate sanitation contribute to an estimated 4 billion cases of diarrhea each year. Diarrheal diseases are estimated to be responsible for 2.2 million deaths and most of these are children under the age of five [2].

Solar disinfection (SODIS) is a simple point-of-use method for reducing the risk of unsafe water [5]. Transparent bottles (preferably PET) are filled with contaminated water and placed in direct

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sunlight for a minimum of 6 h. Following exposure, the water is safer to drink as the viable pathogen load can be significantly decreased due to the action of UV and thermal effects. SODIS is recognised and promoted by the WHO, and there are an estimated 4.5 million regular users worldwide, predominately in Africa, Latin America and Asia [6]; however, there are a number of parameters which affect the efficacy of SODIS, including the solar irradiance, the quality of the water to be treated, and the nature of the contamination (some pathogens are more resistant to SODIS than others). SODIS enhancement technologies may improve the effectiveness without increasing the cost substantially [7].

The SODIS process relies heavily on the solar UV-A which, as received at sea level, is composed of roughly similar portions of both direct and diffuse electromagnetic radiation. Given the diffuse nature of the UV-A and the cylindrical shape of the bottles, the use of concentrating systems based on non-imaging optics with low concentrating factor has the potential to enhance SODIS. The use of compound parabolic collector (CPC) mirrors has been reported to enhance SODIS on sunny and cloudy days due to its good collection of sunlight [8]. Recent work on well water disinfection investigated the disinfection capability of a 25 L CPC reactor to purify water contaminated with *E. coli* K12 [9]. The major advantage of CPCs is that the concentration factor remains constant for all values of sun zenith angle within the acceptance angle limit [8]. Therefore, this technological enhancement can be used to design larger scale systems to treat a greater volume of water for households or small communities.

An additional approach to SODIS enhancement is the use of semiconductor photocatalysis which uses light along with a semiconductor material to produce reactive oxygen species (ROS) that destroy organic pollutants in water and inactivate pathogenic microorganisms [10–14]. Previous work by Fernandez et al. compared suspension and immobilised TiO_2 reactors for the disinfection of water under real sun [15]. That work showed that the TiO_2 suspension reactor was more efficient as compared to the immobilised system for the solar disinfection of water. The TiO_2 (Degussa P25) was immobilised onto glass fibre using SiO_2 as an inorganic binder. Sichel et al. [16] also investigated the use of immobilised TiO_2 for solar water disinfection under real sun. Again the Degussa P25 was immobilised using a SiO_2 binder (Ahlstrom paper). The use of an inorganic binder in the immobilisation protocol will result in decreased photocatalytic efficiency as the binder will block active sites on the TiO_2 surface. While recognising that suspension reactors are more efficient due to the available surface area of catalyst and good mass transfer, the need for post-treatment recovery of nanoparticle TiO_2 is undesirable. Therefore a compromise between reduced efficiency and reduced treatment complexity is reached by utilising immobilised TiO_2. Furthermore, there is no need to utilise an inorganic binder if the nano-TiO_2 is dip or spray coated onto the supporting matrix and heated to elevated temperatures to effect particle to particle cohesion (partial sintering) and particle film adhesion to the support. Indeed such procedures are used for the preparation of high surface area TiO_2 films for 'Gratzel Cells' and the films show meso-porosity with roughness factors up to 1000 [17]. This high surface area has been demonstrated by substantial increases in photocurrent observed on similar nano-particulate films prepared using Degussa P25 (now Aeroxide TiO_2 P25, Evonik) [18]. Sordo et al. [19] reported on a comparison of three types of TiO_2 reactor utilising P25 for solar disinfection i.e. suspension reactor, wall reactor (TiO_2 coated on the outside wall of an inner tube) and a packed bed reactor (TiO_2 coated on Raschig rings). The maximum efficiency was shown by the slurry TiO_2 reactor, due to the optimum contact between bacteria and catalyst. The packed reactor gave an inactivation rate quite close to that of the slurry. They found the wall reactor to be less efficient than SODIS alone, however, the experiments were carried out with *E. coli* in distilled water and it is known that bacteria are prone to environmental stresses including mechanical and osmotic stresses.

In this study, we report on the solar photocatalytic disinfection of water using P25 immobilised on borosilicate glass tubes. The purpose of this work was to test if coating borosilicate glass tubes, as used previously in SODIS reactors, would give rise to an increase in the disinfection efficiency under real sun conditions at pilot scale. Not only that, but the mechanism of photocatalytic disinfection is different to that of SODIS alone and therefore lends advantages in terms of the treatment efficacy. TiO_2 films were produced by dip coating and catalyst loading was 0.5 mg cm^{-2}, determined as optimal for back-face irradiation in previous lab-based experiments [13]. No binder was used in the immobilisation procedure. Experiments were undertaken using 0.9% NaCl to reduce the effect of osmotic stress. Different configurations of coated and uncoated tubes were tested at pilot scale for the disinfection of water under real sun.

2. Materials and methods

2.1. Solar CPC photocatalytic reactor

Modular CPC photoreactors were fabricated at the Plataforma Solar de Almería (Spain) and used for experiments with different configurations i.e. with and without CPC, with and without inner tube, and with and without immobilised TiO_2 photocatalyst. Full details of the photoreactor modules are available elsewhere [20–22]. In brief, five borosilicate glass tubes (50 mm diameter, 1500 mm long) (Schott Glass, Germany) were fitted in the focal line of an aluminium compound parabolic collector (CPC) type made of anodised aluminium (mod. 320G, ALANOD, Germany), acceptance angle (θ_c) of 90° and a concentration factor (C) of 1. The glass tubes were connected to each other and finally to a centrifugal pump (10 W) and a recirculation tank (7 L). The tubes together with the solar CPC mirrors were supported within the photoreactor module frame which was mounted horizontally at an angle of 37°. Where applicable, the CPC reflectors were removed for non-CPC enhanced experiments to be undertaken. During experiments the bacterial suspension was pumped at a flow rate of 2 L min^{-1} through the tubes under examination. During dark control experiments the photo-reactor was covered with opaque black plastic. Each configuration of reactor was tested using one tube and one CPC mirror, with an irradiated surface of 0.2 m^2 and a total volume of treated water of 7 L. The different reactor tube configurations are discussed in Section 2.4.

2.2. Measurement of solar UVA irradiance

Solar UVA radiation was measured with a global UVA radiometer described elsewhere [9]. The radiometer had the same inclination as that of the platform where experiments were conducted.

2.3. Preparation of TiO_2 coated tubes

A custom built automated dip coating apparatus was used to produce TiO_2 (Evonik Aeroxide P25, hereafter referred to as P25) films on the internal surface of borosilicate 1.5 m glass tubes (50 mm diameter, Schott Glass, Germany) and the outer surface of 32 mm diameter borosilicate glass tubes (Scott Glass). To permit efficient coating the 32 mm diameter tube was inserted inside the 50 mm and held in place at both ends of the tubes with ceramic spacers. A 2.5% suspension of TiO_2 in methanol was pumped into the annular space between the glass tubes from the base of the apparatus, with the tubes standing vertical. Upon triggering of an optical level sensor at the top of the tubes, the pump direction

Table 1
Borosilicate glass tube dimensions (mm).

	External diameter	Thickness	Length
External tube (tube A)	50 ± 0.7	1.8 ± 0.15	1500
Internal tube (tube B)	32 ± 0.4	1.4 ± 0.10	1500

was reversed and the flow rate of the suspension was controlled to provide a uniform withdrawal rate down the length of the glass tubes. To complete a coating cycle, the films were dried under a stream of warm air. A series of approximately 60 coating cycles was used to deposit a catalyst loading of 0.5 mg cm^{-2}, as determined previously as the optimum catalyst loading for disinfection for Degussa P25 films under back-face UVA irradiation [13]. Coated tubes were annealed in gas fired kiln at 400 °C for 1 h and allowed to naturally cool to ambient temperature. This annealing stage causes partial sintering of the particles and adhesion to the glass support without the need for binders. XRD analysis before and after annealing of P25 samples to 450 °C showed that the crystallinity and crystallite size for P25 remained unchanged. P25 is a mixture of anatase and rutile (4:1 A:R) with a primary crystallite size of 25–30 nm [23]. The diffuse transmission through the 0.5 mg cm^{-2} TiO_2 on borosilicate plates was determined using a spectral radiometer (Jobin Yvon Gemini 180) with a UVA lamp as the light source (main emission at 365 nm). The transmission was determined to be around 3%.

2.4. Photoreactor tube configurations

The tubes used in the solar reactor were borosilicate glass tubes with two different dimensions as shown in Table 1. Tube A was coated on the inside wall and tube B was coated with catalyst on the outside wall. The different combinations between coated, uncoated tubes and also the use of the CPC produced twelve different test configurations of single and double tubes. To help the reader we have included cross-section schematics of the configurations as shown in Fig. 1. The illuminated volume for the single tube configuration was 2.5 L and, the illuminated volume for the double tube configuration was 1.5 L because the water filled only the annular space between the internal and external tube. For the double tube configurations, test bacterial suspension was placed only the annular space between the internal and external tube, with the inside of the inner tube filled with air. The photographs in Fig. 2 show the TiO_2 coated tubes in the external uncoated–internal coated configuration (a) and the photocatalytic reactor working during disinfection tests (b).

2.5. E. coli growth and enumeration

The bacterial strain used in this work was *E. coli* K-12 (ATCC 23631). A single colony was taken from refrigerated stock and subcultured in 14 mL broth medium (Miller's LB Broth, Sigma–Aldrich, USA). The bacterial suspension was incubated for 24 h at 37 °C with constant agitation on a rotary shaker at 100 rpm to produce a stationary phase culture of ca. 10^9 CFU/mL. *E. coli* suspensions were centrifuged at 3000 rpm for 10 min, the supernatant discarded and the bacterial pellet re-suspended in 14 mL of PBS (phosphate buffer saline) solution. An appropriate inoculum was subsequently added into the photoreactor reservoir to achieve a final cell density of 10^6 CFU/mL.

During the experiments, samples of water (7 mL) were collected from the reactor reservoir at timed intervals during experiments. Bacterial enumeration was carried out by serial dilution of the sample in PBS solution and plating onto Luria agar (Sigma–Aldrich, USA) via a drop count technique. Following overnight incubation at 37 °C, colonies were visually identified and counted manually.

Re-growth analysis was carried out on selected samples. Following overnight storage of water samples taken from the reactor, samples were diluted as described above and plated onto Luria and Endo agar (Sigma–Aldrich, USA).

2.6. Disinfection experiments

All the experiments were carried out under real sun irradiation at the Plataforma Solar de Almería, Spain (latitude 37°N, longitude 2.4°W). The total exposure time for each experiment was 5 h, with exposure started at 10:30 and finishing at 15:30 Spanish local time.

During the re-circulating batch experiments, the reservoir was filled with 7 L of 0.9% NaCl solution. *E. coli* were inoculated into the reservoir 15 min prior to the onset of solar exposure and microbiological sampling was carried out as described before. To investigate the potential for bacterial re-growth, the last two samples of each experiment were maintained in the dark at room temperature with the bacterial concentration determined by the methods described above after 24 h and 48 h. The temperature was measured during all experiments at the sampling time.

2.7. Data fitting and kinetic models

The concentration of viable *E. coli* in each sample taken during SODIS and SPC-DIS experiments was plotted as a function of local time. For a more appropriate comparison of results obtained on different days (with different solar irradiance) the data were evaluated against the accumulated UVA dose as calculated using Eq. (1)

$$\text{Dose}_{\text{UVA}}\,(\text{J m}^{-2}) = \int \text{Irradiance}_{\text{UVA}}\,(\text{W m}^{-2}) \cdot dt\,(\text{s}) \qquad (1)$$

The data were fitted using the Geeraerd and Van Impe Inactivation Model Fitting Tool (GInaFit, version 1.5) [24] using the Dose_{UVA} as the independent variable and found to confirm to a log-linear with shoulder and/or tailing model. Based upon this model, the following outputs from the software were used to assess the relative efficiency of each reactor configuration: the shoulder length (Sl), and the first order rate constant (k), and the log of the residual bacterial concentration ($\text{Log}\,N_{\text{res}}$).

3. Results and discussion

3.1. Dark controls

Dark control experiments were carried out to determine the effect on *E. coli* suspended in saline solution in all reactor configurations (double uncoated tube, single coated tube, single uncoated tube). An opaque sheet was used to cover the reactors to prevent light entering. These tests were designed to check for any detrimental effect due to mechanical stress on bacteria cells at the working flow rate (2 L min^{-1}) and/or due to osmotic stress (saline solution at 0.9% NaCl). There were no negative effects observed due to mechanical or osmotic stress under the experimental conditions stated. There was no significant decrease in the bacterial activity in the dark control experiments. This is in agreement with previous research on solar reactors where the authors used the same isotonic water and pumping conditions [25].

The reported studies for the viability of microorganisms in different types of water vary greatly from one study to another, and even for the same microorganism. Kerr et al. [26] studied the viability of *E. coli* and Teixeira et al. [27] studied the viability of *Pseudomonas aeruginosa*. Both reported that the survival of the microorganisms was higher in high mineral content water than in distilled water. Similar results were reported by Cushnie et al. [28]

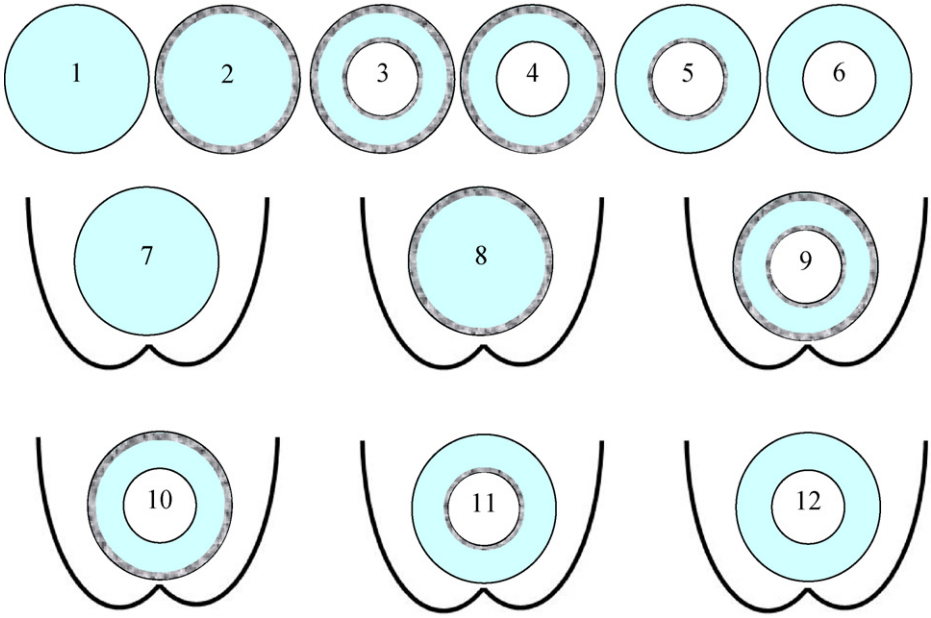

Fig. 1. Schematic cross-section representation of the different reactor configurations tested in the solar reactor, (1)/(7) uncoated single tube without/with CPC; (2)/(8) coated single tube without/with CPC; (3)/(9) coated double tube without/with CPC; (4)/(10) coated external–uncoated internal without/with CPC; (5)/(11) coated internal–uncoated external without/with CPC; (6)/(12) uncoated double tube without/with CPC.

when they investigated the reduction in *E. coli* viability in distilled water and saline. They reported no significant viability change in 0.9% NaCl solution. Liltved and Landfald found a marked reduction in *Aeromonas salmonicida* survivability in natural water samples, even during dark incubation [29]. However, they noted that adding a low concentration of NaCl (0.5 and 0.9%) to the water samples improved the *A. salmonicida* viability either in dark or under irradiation.

Even though there are a number of studies which report a change in microorganism viability under hypotonic water conditions, this specific issue has not been addressed in detail for photocatalytic or photolytic disinfection. In general, researchers have attributed the inactivation of microorganisms in distilled water, under flow conditions, to the synergistic mechano-osmotic effects [25] which are combination of osmotic stress and the stress from fluid movement [16].

3.2. Effect of using CPCs for solar disinfection (SODIS) and solar photocatalytic disinfection (SPC-DIS)

The enhancement effect due to the use of CPC was tested for SODIS in two reactor configurations i.e., uncoated single tube and uncoated double tube; and for SPC-DIS in one reactor configuration i.e., coated single tube, and under different weather conditions. All the experimental results were fitted using the log linear with shoulder and tailing kinetic model [24]. The kinetic parameters, determined using the UVA Dose (Eq. (1)) as the independent variable, are given in Table 2. The temperature increment for systems with or without CPC were almost in the same range (8–10 °C) and the maximum temperature for all configurations never exceeded 32 °C, which is relatively low compared to the reported bactericidal temperature (45 °C) [8,30,31]. According to Blanco et al. [32], the temperature effect can be ignored within the range 12–40 °C for solar disinfection experiments.

For the SPC-DIS experiments in a TiO_2 single coated tube (reactor 2), the use of a CPC (reactor 8) improved the rate of disinfection in cloudy conditions (Fig. 3). The experiments were undertaken in parallel on the same day and therefore can be directly compared in Fig. 3. The data for the kinetic fitting are given in Table 2. The shoulder length (Sl) was the same for both reactor configurations, however, the first order rate constant (k) was greater with the CPC and the log of the residual bacterial concentration ($\mathrm{Log}\, N_{res}$) was lower with the CPC. Navntoft et al. reported that the use of a CPC enhanced disinfection for a static batch reactor, where a 3-log

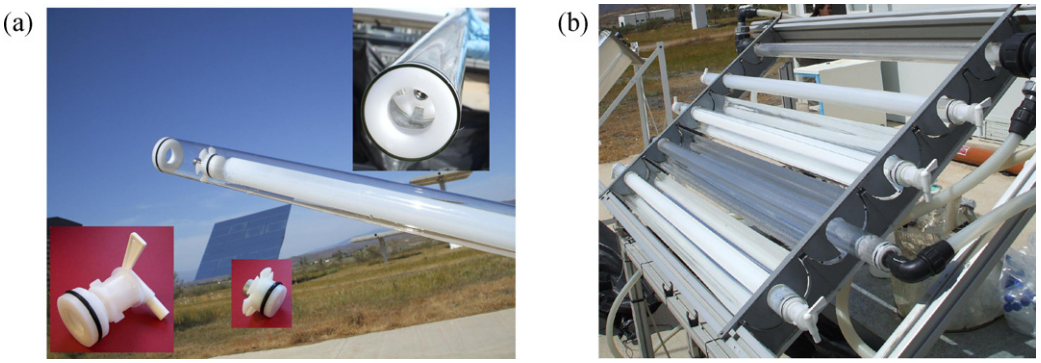

Fig. 2. Photographs showing the double tube configuration with internal tube cap and the valve for external tube (a); and the solar photocatalytic reactor with and without CPC during disinfection tests (b).

Table 2
Effect of CPC on SODIS and SPC-DIS: kinetic parameters found using the Gina-fit tool with the log linear + shoulder + tail model. Data were normalised against the UVA Dose as the independent variable.

Reactor configuration	Parameter		
	Sl (shoulder length) [kJ/m^{-2}]	k (1st order constant) [m^2 kJ^{-1}]	Log N_{res}
1: Uncoated single tube	130 ± 20	0.0093 ± 0.0005	2.6 ± 0.1
2: Coated single tube	60 ± 20	0.0089 ± 0.0006	2.1 ± 0.1
6: Uncoated double tube	70 ± 30	0.0083 ± 0.0004	<DL
7: Uncoated single tube with CPC	90 ± 30	0.014 ± 0.002	1.8 ± 0.2
8: Coated single tube with CPC	60 ± 20	0.0119 ± 0.0009	1.2 ± 0.2
9: Coated double tube with CPC	100 ± 20	0.011 ± 0.002	<DL
10: Coated external–uncoated internal with CPC	50 ± 20	0.0092 ± 0.0006	1.9 ± 0.2
11: Uncoated external- coated internal with CPC	100 ± 20	0.012 ± 0.002	<DL
12: Uncoated double tube with CPC	80 ± 30	0.0094 ± 0.0004	<DL

Note: initial temperatures were between 18 and 22 °C and final temperatures were between 27 and 32 °C.

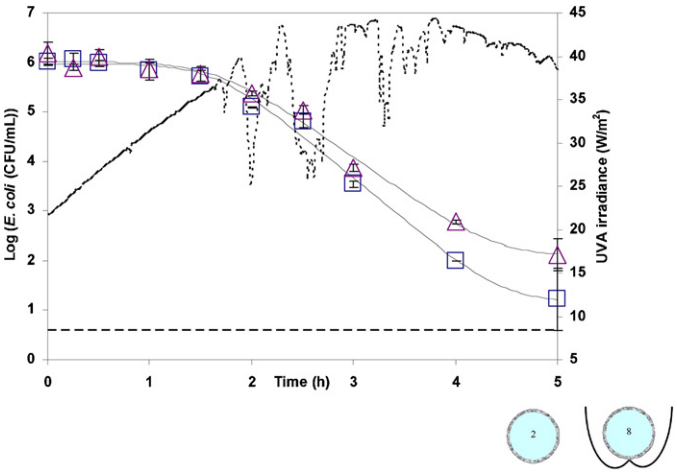

Fig. 3. *E. coli* inactivation for SPC-DIS in saline water (NaCl 0.9%) for a single coated tube with CPC (□), and without CPC (△); solar UVA irradiance (dotted line); *E. coli* detection limit (dashed line). Solid lines represent the fitting curves using the shoulder + log-linear + tail model according to Ref. [24].

decrease was observed without CPC and a 6-log kill with CPC (under cloudy conditions) [8].

The use of CPC also enhanced SODIS for the single uncoated tube reactor (Reactors 1 and 7, Fig. 4). Again the experiments were undertaken in parallel on the same day so the data in Fig. 4 can be compared directly. The addition of the CPC gave a reduced Sl, an increase in k and a lower value for $LogN_{res}$ (see Table 2). The CPC did not yield a marked improvement in the disinfection rate for SODIS in the double uncoated tube configuration (Reactors 6 and 12 in Fig. 5). The experiments were undertaken on the same day in parallel and the data shown in Fig. 5 can be directly compared. The addition of the CPC resulted only in a small increase in the value of k and a small reduction in the value of $Log\,N_{res}$ (see Table 2). The level of enhancement due to the CPC was not as marked as that reported by Navntoft et al. who used a static batch system [8]. The less pronounced effect of the CPC in the re-circulating flow systems may be attributed to the lower residence time under illumination. The percentage of reduction in the irradiation time compared to the static batch system is related to the ratio of the irradiated volume (V_i) to the total volume (V_T) by the following equation:

$$\text{reduction}\,\% = \left[1 - \frac{V_i}{V_T}\right] \cdot 100\% \quad (2)$$

For the single tube configuration, the irradiation time was reduced by 64% with CPC, while for the double tube configuration the reduction was around 79% with CPC. This reduction in the irradiation time means also a reduction in the accumulated energy by the same degree under similar UV intensities. The improvement found with the CPC is always attributed to the increased amount of accumulated energy per unit volume as compared to systems without CPC. The amount of accumulated energy in flow systems is lower for systems with or without CPC and the differences are less marked as compared to the static batch systems.

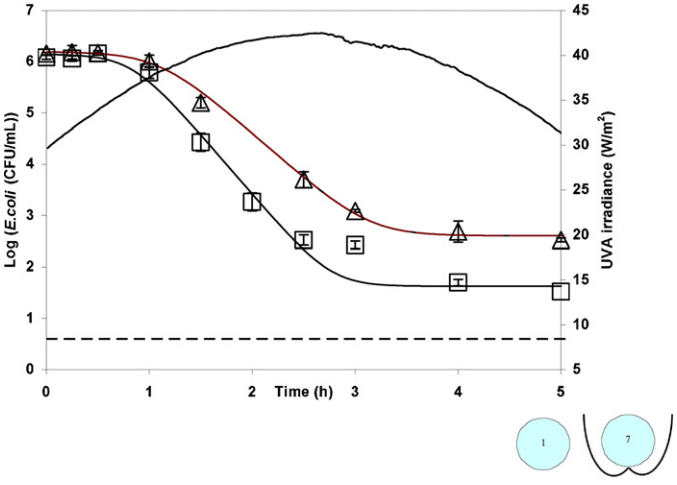

Fig. 4. *E. coli* inactivation using SODIS in saline solution (NaCl 0.9%) with a single uncoated tube with CPC (□), without CPC (△), UVA irradiance (solid line); *E. coli* detection limit (dashed line). Solid lines represent the fitting curves.

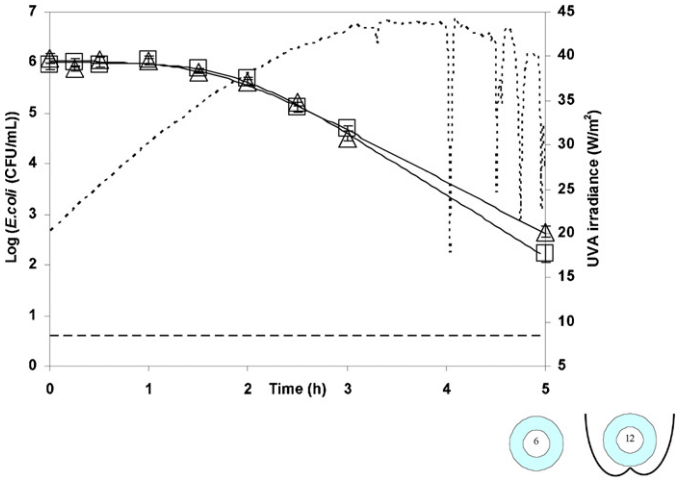

Fig. 5. *E. coli* inactivation using SODIS in saline water with a double uncoated tube with CPC (□), without CPC (△), UVA irradiance (dotted line), *E. coli* detection limit (dashed line). Solid lines represent the fitting curves.

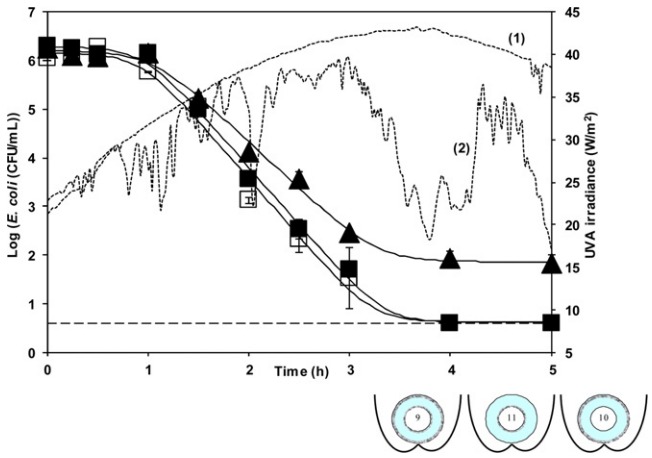

Fig. 6. *E. coli* inactivation in the CPC reactor with the following reactor configurations: double coated (□), coated internal with uncoated external (■), and coated external with uncoated internal (▲). UVA irradiance (dotted lines 1 and 2). UVA(1) relates to solid symbols and UVA(2) relates to empty symbols. *E. coli* detection limit (dashed line). Solid lines represent the fitting curves.

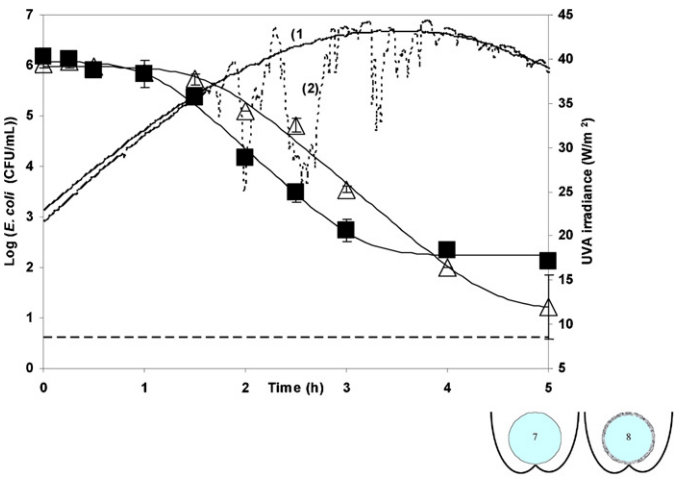

Fig. 8. *E. coli* inactivation in solar CPC reactor with reactor configurations as follows; single coated (△) and single uncoated (■). UVA irradiance (dotted lines 1 and 2). UVA(1) relates with solid symbols and UVA(2) relates with empty symbols. *E. coli* detection limit (dashed line). Solid lines represent the fitting curves.

3.3. Comparison between the different configurations with CPC

As the use of the CPC was found to enhance the rate of disinfection, any further work was undertaken in reactor configurations with CPCs. The reactor configurations tested were; 7: single uncoated tube with CPC, 8: single coated tube with CPC, 9: coated double tube with CPC, 12: double uncoated tube with CPC, 10: coated external with uncoated internal tube with CPC, and 11: uncoated external with coated internal tube with CPC.

For ease of comparison, the figures show experiments against real time on very similar days, in relation to solar irradiation and environmental temperature. These results are discussed taking into account the solar UVA irradiance received at any time (right *Y*-axis in Figs. 6–9). The kinetic modelling of the data was done using the solar UVA dose as the independent variable and the data are given in Table 2.

From Fig. 6, it is seen that the rate of disinfection and residual concentrations are similar for the double coated tube (reactor 9) and the internal coated external uncoated tube configurations (reactor 11). From the kinetic modelling normalising to UVA dose (Table 2), the shoulder length is the same for both, and both achieve $Log\,N_{res}$ below the detection limit. However, the first order rate constant k was found to be similar for reactors 9 and 11 (0.011 $m^2\,kJ^{-1}$ and 0.012 $m^2\,kJ^{-1}$ respectively). From the same figure, the coated internal with uncoated external tube was tested on the same day as the coated external uncoated internal tube. The former gave a better *E. coli* inactivation efficiency. The coated internal uncoated external configuration has an advantage over in that it makes use of all the available UV light for photolytic inactivation i.e., SODIS and photocatalytic inactivation (SPC-DIS). However, back-face irradiation (where the catalyst is immobilised on the outer tube) has the advantage of not being limited by light losses due to absorption or scattering by contaminants in the water. The coated double tube (reactor 9) showed a superior performance as compared to the coated external–uncoated internal (reactor 10) in terms of a higher k value and lower $Log\,N_{res}$ value (Table 2). Diffuse transmission measurements on the 0.5 mg cm^{-2} P25 films showed only 3% transmission in the UVA domain. It is possible that these transmitted photons lead to some excitation of the inner coated tube

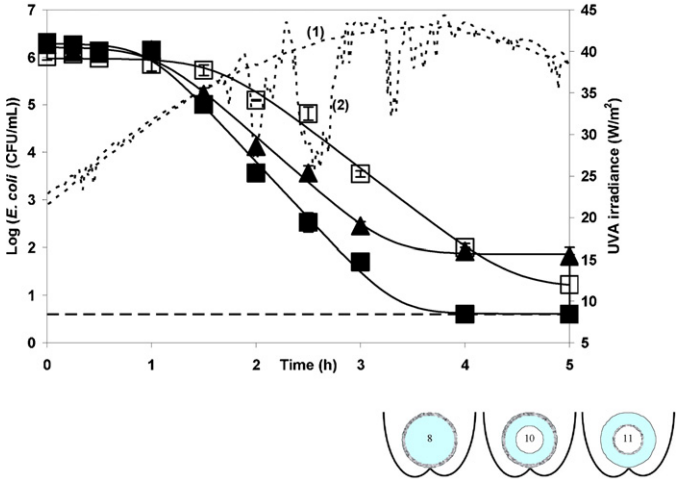

Fig. 7. *E. coli* inactivation in the CPC reactor with the following catalyst configurations: single coated (□); coated external with uncoated internal (▲); and coated internal with uncoated external (■). UVA irradiance (dotted lines 1 and 2). UVA(1) relates with solid symbols and UVA(2) relates with empty symbols. *E. coli* detection limit (dashed line). Solid lines represent the fitting curves.

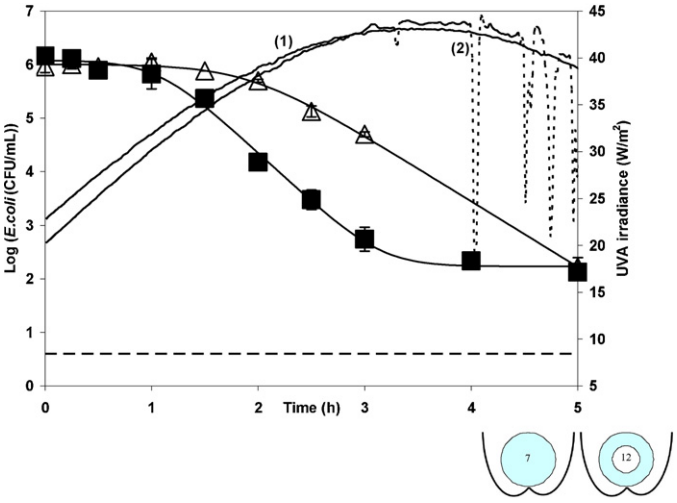

Fig. 9. *E. coli* inactivation in solar CPC reactors. Single uncoated tube (■) and double uncoated tube (△). UVA irradiance (dotted lines 1 and 2). UVA(1) relates with solid symbols and UVA(2) relates with empty symbols. *E. coli* detection limit (dashed line). Solid lines represent the fitting curves.

for reactor configuration 9, or perhaps, the TiO_2 on the inner tube may act as a site for adsorption of bacteria resulting in a longer residence time within the irradiated volume of the reactor, and potential attack by free ROS.

Fig. 7 shows that the efficiency of the single coated tube (reactor 8) was intermediate between the coated internal uncoated external tube (reactor 11) and the coated external uncoated internal tube (reactor 10) according to the residual bacterial concentration. The solar UVA irradiance on both days (Fig. 7) was very similar for the first 2 h.

The same behaviour in solar irradiance was observed for the experimental data given in Fig. 8 from which it can be seen that the single coated tube configuration (reactor 8) was more effective than the uncoated tube (reactor 7).

It can be seen from Figs. 7 and 8 that the single uncoated tube (reactor 7) was less efficient than the coated external uncoated internal tube (reactor 10). Comparison between the single uncoated (reactor 7) and double uncoated (reactor 12) showed that the residual concentration was almost the same for similar weather conditions (Fig. 9); however, the single uncoated tube showed a tail in the disinfection and did not reach the detection limit.

We can compare the order of efficiency for the different configurations tested based upon the data from Table 2 which has been normalised using the UVA dose as the independent parameter. If we consider only those systems which, according to the kinetic fitting, achieve a $Log\,N_{res}$ value below the detection limit, then the order of efficiency based upon the first order rate constant is as follows:

Reactor 11: uncoated external- coated internal tube with CPC	$k = 0.012\ m^2\,kJ^{-1}$
Greater than or equal to;	
Reactor 9: double coated tube with CPC	$k = 0.011\ m^2\,kJ^{-1}$
Greater than or equal to;	
Reactor 12: uncoated double tube with CPC	$k = 0.0094\ m^2\,kJ^{-1}$

The error is such that there is no significant difference between the k values for reactor configurations 11 and 9, and no significant difference between the k values for reactor configurations 9 and 12. It would appear that there is no marked enhancement due to the presence of the photocatalyst, however, there is a significant difference in the mechanisms involved between SODIS and SPC-DIS (vide infra).

3.4. SODIS of E. coli cells which survived SPC-DIS treatment

The SPC-DIS in the coated external uncoated internal tube configuration can represent a highest stress conditions for the bacteria i.e. photocatalysis with photolysis. In order to test if bacteria, which were subjected to SPC-DIS and survived, had developed a resistance, or to see if there was a resistant sub-population, a further experiment was performed. The *E. coli* cells that survived as the residual population following treatment in this reactor were cultured and harvested again. This culture was then subjected to SODIS in a static batch system using a single uncoated tube reactor configuration. As shown in Fig. 10, the *E. coli* cells did not develop any resistance and they behaved in the same way as the fresh cells previous experiments undertaken in the static batch reactor.

SODIS with CPC alone (Fig. 10) appears to show the fastest inactivation of *E. coli* overall; however, this experiment was carried out in a static batch reactor i.e. with no flow or forced convection, and the total volume treated was 2.5 L which, was continuously exposed to solar irradiation. The total volume in the flow-reactor experiments was 7.0 L with a flow rate of 2 L min^{-1} (Figs. 4, 5, 8 and 9), and the irradiated volume was 2.5 L for a single tube reactor and 1.5 L for a double tube reactor. We demonstrated in our previous work [22] that SODIS inactivation from approximately 10^6 CFU/mL

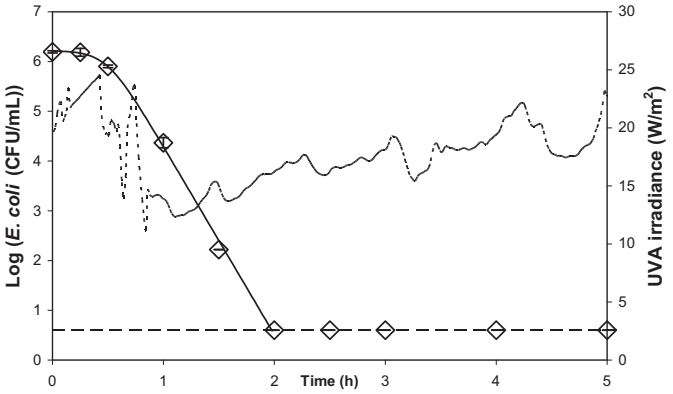

Fig. 10. SODIS inactivation of recovered *E. coli* using a single uncoated tube with CPC reactor under static conditions in distilled water (◊). UVA irradiance is presented with dotted line. *E. coli* detection limit (dashed line). Solid line represents the fitting curve.

to below the detection level (4 CFU/mL) for *E. coli* K-12, is a function of the total uninterrupted dose delivered to the bacteria and that the minimum dose should be >108 kJ/m^2 in the spectral range of 0.295–0.385 mm. For complete inactivation to below the limit of detection, this dose needs to be received regardless of the incident solar UV intensity (between 14 and 40 W/m^2) and needs to be delivered in a continuous and uninterrupted manner. This was illustrated by a continuous flow system in which bacteria were not fully inactivated (residual viable concentration ~10^2 CFU/mL) even after 5 h of exposure to strong sunlight and a cumulative dose of >108 kJ/m^2 [22]. This work showed that inactivation is not only dependent on the dose received but on the way in which the dose is delivered. If the operational parameters are set such that the microbial pathogens are repeatedly exposed to sub-lethal doses of solar radiation followed by a period within which the cells have an opportunity to recover or repair, complete inactivation may not be achieved [22], as we found (Figs. 4, 5, 8 and 9).

3.5. Discussion

In 1999 Vidal et al. published one of the first pilot plant studies that utilised TiO_2 solar photocatalysis for water disinfection wherein they deployed the TiO_2 as a suspension. These authors constructed a low-cost compact parabolic concentrator (CPC) prototype to harvest solar radiation for water disinfection. This solar photo-reactor had 4.5 m^2 of CPC aperture and was oriented towards the equator and tilted at local latitude to maximise the available solar radiation for long exposure periods. This system demonstrated a 5-log reduction in the concentration of *E. coli* and almost total removal of *Enterococcus faecalis* (initial concentration 10^2–10^4 CFU/mL) with 0.5 g/L TiO_2 suspension and 30 min of solar irradiation (where the average solar UV irradiance was 25 W/m^2) [33].

The use of immobilised photocatalyst systems (as reported here) removes the need for post treatment recovery of the catalyst, however, suspension systems are more efficient in terms of photocatalytic rate [12]. It is well know that the main problems of immobilised systems, as compared to suspensions, are the reduced surface area of catalyst available for reaction and the mass transfer limitations within the reactors. Immobilised systems have been shown to inactivate several common bacteria (*Serratia marcescens*, *E. coli*, and *Streptococcus aureus*) with UV-C lamps or with sunlight in less than 10 min [34]. Sichel et al. observed complete inactivation of *E. coli* K-12 (initial concentration of 10^6 CFU/mL) and fungi spores of *Fusarium solani* (initial concentration of 10^3 CFU/mL) under solar exposure in a flow-CPC reactor with TiO_2 immobilised on Ahlstrom paper [35]. A reduction of *Cryptosporidium parvum* oocysts viability

from 98.3% (±0.3%) to zero was observed after 24 h of exposure to sunlight with TiO_2 fixed in cylindrical line of black silicone adhesive bathroom sealant [36]. Gelover et al. reported on the fabrication of a simple a home-made low cost solar reactor (solar box). They filled it with real water and found complete disinfection of total coliforms only when immobilised TiO_2 (supported over cylindrical glass pieces) was introduced into the solar box. They also eliminated the bacteria re-growth after the photocatalytic treatment [37]. A similar result was also observed by Rincón et al. using *E. coli*, *Bacillus subtilis* and wastewater containing a broad bacterial community. They investigated the inactivation kinetics using another configuration reactor with UV-lamps and TiO_2 coated on fibre glass [38].

In comparison to suspension systems, there are relatively few pilot plant scale studies that use immobilised photocatalyst for water disinfection. Most studies are based on small scale (i.e. laboratory) systems. However, there has been steady improvement of solar disinfection using supported TiO_2 on resistant flexible materials, such as cylinders, pills, balls, mesh, etc. Like for example, Van Grieken et al. reported about the inactivation kinetics of *E. coli* and *Enterococcus fecalis* using TiO_2 suspensions and TiO_2 immobilised onto the glass wall of the annular reactor with a total volume of 1 L. They observed that the bacterial inactivation with the immobilised catalyst required longer irradiation times in comparison with the TiO_2 suspension for both bacteria, attributed to the lower catalyst surface [39]. Bigger scale disinfection tests have been done at Plataforma solar de Almeria using CPC reactors under sunlight. This work showed similar results wherein the inactivation of *E. coli* was more efficient with a suspension as compared to using TiO_2 immobilised on Ahlstrom fibreglass [16]. Marugán et al. reported the limitations of porous TiO_2/SiO_2 photocatalysts to inactivate *E. coli* K-12 due to restrictions in the access of the bacteria to the catalyst surface; leading thus, reduced values of the kinetic and pseudo-adsorption constants [40]. However, Rincón et al. reported similar efficiencies for the inactivation of *E.coli* using TiO_2 immobilised on Nafion® membranes as compared to suspensions of TiO_2 [41].

The key problem for suspension systems is the separation of TiO_2 nanoparticles (or sub-micron agglomerates/aggregates) from the water following treatment. Some contributions suggest TiO_2 recovery using the high mass density of titania ($3.2\,g\,cm^{-3}$). The catalyst recovery can be done by settling aggregates of TiO_2 particles, i.e. taking advantage of their high tendency to react with water and any chemical species [42].

The main problem with immobilised photocatalyst systems is the reduced rate of photocatalytic inactivation due to mass transfer limitations. Other factors will also affect the efficiency of these systems including: (i) the contact time or residence time, which is given by the reactor flow rate; (ii) the total volume of water to be treated; (iii) the physico-chemical characteristics of the water; (iv) aging or durability of the coating, which is also affected by the hydrodynamic conditions of the system; (v) fouling of the photocatalyst. Therefore, it remains that there is much work to be done in this field.

There is a broad consensus that immobilising TiO_2 on a solid substrate will reduce the surface area available for reaction and limit the mass transfer of reactants to the photocatalyst surface [43]. Thus immobilised systems require more contact time than suspension systems, and consequently a larger footprint to achieve the same disinfection levels for a given flow rate. However, the absence of a need to separate the photocatalyst is the advantage of immobilised systems, increasing their simplicity in design and operation. We have previously tested P25 films in a stirred tank reactor [43] which is a much more aggressive environment in terms of fluid mechanics than the flow reactors tested here, and we observed no catalyst stripping over prolonged testing periods. No catalyst stripping was observed from the glass tubes in these experiments.

In this work we observed that there was not a marked difference between SODIS and SPC-DIS using the double tube reactor with CPC (with or without immobilised TiO_2 respectively). However, it must be noted that the mechanisms for SODIS and SPC-DIS are different which presents advantages for SPC-DIS. For SODIS (disinfection using sunlight alone), studies have demonstrated the effects of key operational parameters such as light intensity and wavelength, solar exposure time, availability of oxygen, turbidity, and temperature [44]. The mechanism of SODIS is understood to involve a number of biocidal pathways based upon absorption of UVA radiation and thermal inactivation. Direct UVA exposure can induce cellular membrane damage and delay microbial growth [45]. The action of UVA has also been attributed to the production of reactive oxygen species (ROS) which are generated from dissolved oxygen in water [46] and the photosensitisation of molecules in the cell, and/or any naturally occurring dissolved organic matter that will absorb UVA, to induce photochemical reactions [30]. At temperatures below 40 °C, the thermal effect is negligible with UVA inactivation mechanisms dominating the inactivation process. In most photocatalytic disinfection studies, the hydroxyl radical is suggested to be the primary species responsible for microorganism inactivation; however, some papers do report involvement of other ROS, such as H_2O_2, $O_2^{\bullet -}$ [47,48]. These ROS can cause fatal damage to microorganisms by disruption of the cell membrane or by attacking DNA and RNA [10]. Other modes of action TiO_2 photocatalysis have been proposed, including damage to the respiratory system within the cells [49] and loss of fluidity and increased ion permeability in the cell membrane [48]. Detailed spectroscopy-based studies attributed cell death to lipid peroxidation of bacterial cell membrane [47,48]. The peroxidation of the unsaturated phospholipids contained in the bacterial cell membrane results in loss of respiratory activity [50] and/or leads to a loss of fluidity and increased ion permeability [48]. It has also been suggested that cell membrane damage can open the way for further oxidative attack of internal cellular components, ultimately resulting in cell death [50].

Gelover et al. [37] reported regrowth of coliforms was observed following SODIS while no regrowth was observed following solar photocatalytic disinfection with TiO_2. Radical production via photocatalysis significantly contributes to irreversible injury leading to more efficient disinfection than found with solar UV alone [51]. Also, photocatalysis has been demonstrated to inactivate more resistant species including the oocysts of *Cryptosporidium parvum*, while little affect was attributed to UVA only [52]. The rate of inactivation for *E. coli* was not markedly different in this study for SODIS and SPC-DIS in the double tube reactor with CPC; however, it is known that *E. coli* is inactivated by SODIS and it may be a 'soft' target for comparing the effectiveness of SODIS vs SPC-DIS. The photocatalytic systems present advantages in terms of the non-recovery of inactivated organisms and the inactivation of SODIS resistance organisms. Furthermore, if the photocatalyst is activated via back-face irradiation, as in the double coated tube configuration, then absorption and scattering of light by water contaminants should not affect the efficiency. Further work will concentrate on the improvement of photocatalytic reactor design for increased illuminated catalyst area to water volume ratio and increased mass transfer.

While it is recognised that pumped-in treated water supplies should be an ultimate goal for the provision of safe water for the poor, it remains that many millions remain without access to improved water resources for drinking. Point-of-use systems which utilise low cost technologies could help to address the provision of safer drinking water for developing countries, particularly in rural areas. The use of solar energy for the disinfection and treatment of water is ideal as solar light is widely and freely available. It has been demonstrated that the use of CPCs and photocatalysis can lead to

the enhancement of the solar disinfection of water. If such systems were to be deployed in developing countries for the disinfection of water, the enhancement technologies must not add substantially to the cost of treatment. Furthermore, there are a number of issues which should be addressed before the deployment of such systems. For photocatalysis, catalyst fouling and longevity must be studied in systems under real field conditions. If pumping systems are to be used as in the re-circulating flow reactors discussed here, then the power and maintenance requirements of the pumps must be addressed. As the efficacy of the process depends on the UVA irradiance, the use of low cost UVA sensors may allow for the automated control of the process, therefore providing some quality assurance for the user. It should be noted that the reactor systems tested in this work where essentially SODIS reactors with photocatalyst added by coating of the glass tubes. This is obviously not the optimal configuration for a photocatalytic reactor and improvements in the design of SPC-DIS reactors could lead to enhanced efficiencies such as those observed in lab-scale studies. Furthermore, developments in the area of visible light active photocatalytic materials may increase the efficacy under solar irradiation. The use of solar photocatalytic reactors may also present additional benefits over SODIS alone for the destruction of toxic organic chemicals found in water and for the inactivation of SODIS resistant microorganisms.

4. Conclusions

Solar photocatalytic (SPC-DIS) and photolytic disinfection (SODIS) of water were tested under flow conditions using different reactor configurations and under different weather conditions. The use of compound parabolic collectors improved the SODIS and SPC-DIS of water, however, the improvement was less significant compared to the improvements reported previously for SODIS in static batch reactors.

All *E. coli* inactivation vs time data showed good fitting using the log linear model with shoulder and/or tail. The kinetic parameters were determined using the UVA dose as the independent variable and the configurations were compared for *E. coli* inactivation efficiency based on the log of the residual concentration ($Log\, N_{res}$) and the first order rate constant (k). Three reactor configurations showed a residual bacterial count below the detection limit and they were compared based upon the first order rate constant. The concentric tube arrangement (a tube within a tube) with CPC was the most effective configuration. The following order was found for k where coated refers to TiO_2 coating and the equals sign indicates no significant difference; uncoated external- coated internal $\geq$ double coated tube $\geq$ uncoated double tube. It is known that *E. coli* is inactivated by SODIS and it may be a 'soft' target for comparing the effectiveness of SODIS vs SPC-DIS. Nevertheless, photocatalysis presents advantages in terms of the non-recovery of inactivated organisms and the inactivation of SODIS resistance organisms.

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